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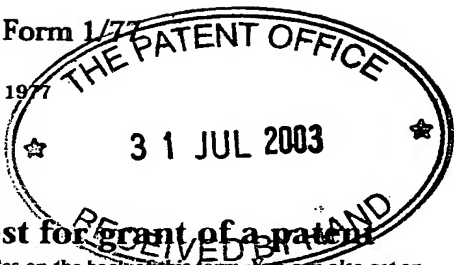
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Request for grant of a patent

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31 JUL 2003

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2. Patent application number <i>(The Patent Office will fill in this part)</i>	0317989.2		
3. Full name, address and postcode of the or of each applicant <i>(underline all surnames)</i>	ROCKWOOL INTERNATIONAL A/S 584 Hovedgaden DK-2640 Hedehusene Denmark		
Patents ADP number <i>(if you know it)</i>			
If the applicant is a corporate body, give the country/state of its incorporation	DK	671188006	
4. Title of the invention	Mineral Fibre Products		
5. Name of your agent <i>(if you have one)</i>	Gill Jennings & Every		
"Address for service" in the United Kingdom to which all correspondence should be sent <i>(including the postcode)</i>	Broadgate House 7 Eldon Street London EC2M 7LH		
Patents ADP number <i>(if you know it)</i>	745002	✓	
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7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application		Date of filing <i>(day / month / year)</i>
8. Is a statement of inventorship and of right to grant of a patent required in support of this request? <i>(Answer 'Yes' if:</i> a) <i>any applicant named in part 3 is not an inventor, or</i> b) <i>there is an inventor who is not named as an applicant, or</i> c) <i>any named applicant is a corporate body.</i> <i>See note (d))</i>	YES		

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Description

14

Claim(s)

3

Abstract

1

Drawing(s)

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

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NO

11. For the applicant
Gill Jennings & Every

I/We request the grant of a patent on the basis of this application.

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12. Name and daytime telephone number of person to contact in the United Kingdom

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Mineral Fibre Products

This invention relates to mineral fibre products which are of particular value for use as fire protection or in other environments where the fibres have to resist very high temperatures, for instance above 700°C and often above 900°C or above 1000°C. Fibres frequently used for such products at present include the fibres often referred to as rock fibres, slag fibres or stone fibres.

The fibres are formed of a silicate network which, as is well known, is a tetrahedral network formed predominantly by silicon, and optionally aluminium, atoms bridged by oxygen atoms, and the network also retains various other atoms, frequently including calcium, magnesium and iron, and others. It is known that the properties of the fibres depend on the chemical analysis of the fibres, and thus on the nature of the network and the other atoms retained in the network.

When the temperature of an assembly of the fibres exceeds T_g (the glass transition temperature) the fibres adopt a visco-elastic state with the result that they may tend to start to lose their individual fibrous form, and in particular there may be some flow at the surfaces of the fibres, leading to fusion at the intersections of fibres. At higher temperatures, the flow becomes more serious and the fibres may fuse into a much smaller volume than was occupied by the original assembly of fibres. At T_c (the crystallisation temperature) the tetrahedral network will tend to reorganise into a crystalline structure. As the temperatures increase still further, the crystals will start to melt at T_m , the melting temperature. For a typical rock fibre T_g may be around 650-700°C eg 680°C, T_c around 820-900°C eg 850°C and T_m around 1,000 to 1,100°C eg 1050°C.

The mechanisms by which the fibrous assembly eventually collapses as the temperature increases can therefore be seen to be rather complex.

In practice, what is actually required is that the fibres should maintain as much as possible of their fibrous form to as high a temperature as possible. It is therefore conventional to report the temperature at which any particular type of fibre is likely to fail. For instance
5 collapse or sintering temperatures are commonly quoted as an indication of the temperature at which the fibrous nature of the fibres is likely to be lost sufficiently to impair their fire protection and other insulation
10 properties. Numerous publications therefore quote collapse or sintering temperatures.

It is known that the chemical composition of the fibres influences sintering and collapse temperatures. For instance, numerous publications indicate that iron and
15 other elements can increase sintering temperature.

In an attempt at providing fire protection to higher temperatures, it is known to add various endothermic compounds into mineral fibre products which are intended for fire protection, so that the compound will tend to
20 absorb heat energy and thus delay the onset of collapse or sintering, despite the external temperature being higher than the fibre might have been able to withstand in the absence of the added material. Numerous publications therefore propose various additives or other ways of
25 increasing protection at high temperatures.

It is also known that, even in the absence of endothermic additives, the conditions under which the fibre product is exposed to increasing temperature may significantly influence the performance of the fibres. In
30 particular it is known that when a thick slab of bonded, high density, mineral wool is exposed to high temperatures, the core may collapse due to sintering to leave a void (with the result that the fire protection properties are unsatisfactory) whilst the outer surface may remain
35 reasonably fibrous (so that the product may be assumed, wrongly, to have good fire protection properties).

A particular problem arises with fire doors and sandwich panels, namely semi-sealed or sealed products containing bonded mineral wool between sheets of material which prevent free access of air. It is found that these
5 may fail due to sintering at a temperature lower than would be expected having regard to the known failure temperatures of the mineral wool.

These failures of bonded mineral wool and of sealed or semi-sealed products have generally been assumed to be
10 caused by the exotherm created by the combustion of organic bonding agent in the mineral fibre product, this exotherm giving local heating so as to cause localised increase in temperature, and therefore sintering.

The selection of the chemical content of mineral
15 fibres now has to take account of numerous factors including ability to form the fibres by conventional techniques, cost and availability of raw materials, biodegradability of the fibres, and weather resistance of the fibres and, as discussed above, the sintering
20 properties of the fibres.

It would be desirable to be able to increase the temperature to which fibrous products can be exposed without the fibres tending to collapse to such an extent that their fire protection and other insulation properties
25 deteriorate. In particular, it would be desirable to be able to modify a fibrous product so that the temperature at which deterioration becomes significant is raised, and it would be desirable to be able to do this without having to add endothermic compounds or other additives to protect the
30 fibres from the ambient high temperature.

Mineral fibre products according to the invention comprise fibres formed of a silicate network comprising silicon, calcium, magnesium, iron, aluminium and oxygen atoms, as is conventional. In the invention the fibres are
35 characterised by the fact that at least 70% of the iron is present as ferric iron, and by the fact that the fibres have a core which is surrounded by an outer surface layer

less than $1\mu\text{m}$ thick in which the concentrations of calcium atoms and magnesium atoms are both at least 1.5 times the concentrations of calcium atoms and magnesium atoms in the total fibres.

5 We find that modifying fibres so that the iron is wholly or substantially ferric and there is an outer surface layer which is enriched in calcium and magnesium results in the fibres being able to withstand higher temperatures before sintering or collapse occurs. Although
10 it is naturally desirable that all the fibres should be modified in this way, it is not essential provided that the proportion of fibres which is modified in this way is sufficiently high to impart improved temperature resistance to the entire product. The fibres having the surface layer
15 should be distributed substantially uniformly (in all three dimensions) through the batt or other product in order that the batt has substantially uniform temperature resistance throughout its volume.

20 In practice it is usually simplest to subject all the fibres which it is intended to modify to the conditions that will provide the modification, without checking that each and every fibre is modified.

The provision of the surface layer which is on each modified fibre and which is enriched in calcium and
25 magnesium is preferably achieved by outwards diffusion to the surface of the fibre of calcium and magnesium from within the network of which each fibre is formed. As a result, the layer on a fibre preferably merges with the core of the fibre and has been formed by outwards diffusion
30 of calcium and magnesium ions to the surface of the fibre.

The enriched outer layer may comprise calcium and magnesium predominantly in the form of their oxides, but preferably the enrichment is as a result of the layer comprising crystals of calcium magnesium silicates
35 (optionally also including other atoms such as iron and aluminium), and in particular comprises crystals of diopside and/or augite.

By saying that the concentration of calcium and magnesium in the layer is at least 1.5 times the concentration in the total fibre we mean that, when the fibre is subjected to SNMS depth profile analysis and the concentration of calcium and magnesium is plotted from the outermost surface inwards, the peak concentrations of calcium and magnesium which are observed in the outer layer are at least 1.5 times the substantially uniform concentration of calcium and magnesium that will be observed throughout the remainder of the fibre. This substantially uniform concentration is substantially the chemical analysis of the total fibre.

Preferably the concentration of each of calcium and magnesium in the outer layer is at least 2, 3 or 4 times, and may be as much as 5 times or even up to 6 or 7 times or more, the concentration in the total fibre. In particular, although good results are obtained with calcium concentrations which are, for instance, 2 to 4 times the concentration in the remainder of the fibre, it seems desirable for the magnesium enrichment to be particularly high, for instance being 3 to 6 times the magnesium concentration in the total fibre.

The surface layer can be regarded as the layer over which the calcium and magnesium concentrations are measurably higher than the concentrations in the total fibre and this surface layer is below $1\mu\text{m}$ thick and is usually below $0.5\mu\text{m}$ thick. Often the surface layer is 0.1 or 0.2 to $0.5\mu\text{m}$ thick. The peak concentrations discussed above are usually in the outermost 0.01, and often 0.05, μm of the fibre. Accordingly the core (ie excluding the 0.5 or $1\mu\text{m}$ surface layer) will normally have a substantially uniform concentration of most or all of the elements in the fibre, and the highest concentrations of calcium and magnesium are in the outermost $0.05\mu\text{m}$ or $0.1\mu\text{m}$, with transitional concentrations in the intermediate region between the peak concentration and the core inwards of 0.05 or $1\mu\text{m}$.

It seems that the presence of the enriched magnesium and calcium layer in the surface prevents or reduces the initiation of melt flow which at the surfaces and intersections of fibres, which is probably the first step
5 towards sintering and collapse. Thus, the provision of the enriched calcium and magnesium layer results in an increase in the temperature at which surface melt flow starts to occur and results in an increase in the temperature at which collapse and sintering will occur.

10 There is some evidence that iron also may be present in the outer surface layer in an amount greater than the amount in the remainder of the fibre, for instance in an amount of 1.1 or 1.2 up to 2 or more times the amount of iron in the remainder of the fibre.

15 However the predominant characteristic of the iron in the fibre is that it must be substantially ferric and thus at least 70% of the iron in the fibre must be ferric and usually at least 80, 90 or, preferably, at least 95% of the iron is ferric. It seems that ideally substantially 100%
20 of the iron would be ferric. These percentages are based on the weight of iron.

The reason why the iron should be wholly or predominantly ferric is that we believe the formation of the calcium-enriched and magnesium-enriched surface layer
25 is promoted by a mechanism which includes the oxidation of ferrous to ferric.

In particular, the surface layer is best formed by exposing fibres formed of a silicate network containing ferrous ions to oxidising conditions at a temperature at
30 which ferrous ions are oxidised in the fibres to ferric ions.

It is well known that the silicate network of mineral fibres such as rock, stone and slag fibres is a tetrahedral network formed predominantly by silicon, and optionally
35 aluminium, bridged by oxygen atoms and also containing calcium, magnesium and iron atoms, and often small amounts of alkali metal and other atoms such as titanium. The

calcium and magnesium atoms are thought to be held within the network by relatively weak bonding to oxygen atoms of the network. This is stable under low and moderate temperatures.

5 However, if the temperatures increases (for instance to near or above T_g) when the surface of the fibres is exposed to oxidising conditions, we believe the calcium-oxygen and magnesium-oxygen bonds tend to break with consequential oxidation of ferrous to ferric and with the
10 release of calcium and magnesium cations to diffuse through the solid network of the fibre towards the surface, which is under oxidising conditions. This release and diffusion does not seem to occur when the surface is not exposed to oxidising conditions.

15 The calcium and magnesium cations appear to be oxidised at the surface initially to form oxides, and it appears that they can then interact with the silica to form crystals such as diopside and/or angite, especially when the temperature is sufficiently high, (usually above T_g).

20 In order to prevent the entire tetrahedral network crystallising, with subsequent severe effects on fibre properties such as brittleness, the temperature must not be too high.

 Accordingly, formation of the desired surface layer
25 seems to depend on both the equilibrium between external oxidising conditions and the calcium and magnesium cations which diffuse to the surface, and on the equilibrium between ferrous and ferric which occurs when the calcium-oxygen and magnesium-oxygen bonds break.

30 Other atoms in the network have a lower tendency to break their oxygen linkages to the network. Thus although some alkali metal may sometimes leave its oxygen bonds behind and migrate to the surface, the amount is usually low. Aluminium and titanium diffuse much less and oxygen
35 diffuses hardly at all, below T_g .

 In order to optimise the mechanism, the fibres should initially contain sufficient ferrous ion to enter into the

equilibrium and so in practice should have at least 2% by weight ferrous, and usually at least 3 or 4% by weight ferrous.

We are unaware of anyone having proposed previously,
5 in the context of mineral fibres, any of the mechanisms and effects which are achieved in the invention. However we are now aware of a publication by Burkhard in Journal of Petrology, 2001, volume 42, pages 507 to 527 and we believe that this confirms our understanding of the chemical
10 mechanism involved in the invention. Burkhard is not concerned with fibres but is concerned with the crystallisation and oxidation of volcanic glass and reports experiments conducted on glass chunks and powder. These experiments show, for instance, the formation of a surface
15 layer which is 15 to 20 μ m thick and which has enhanced concentrations of calcium and magnesium and which is described as being formed of crystallised pyroxene. Depthwise crystallisation of this type would be unacceptable in mineral fibres.

20 The heating which is necessary to achieve oxidation of the fibres does tend to cause some embrittlement of the fibres because of the initiation of a tendency to crystallisation within the silicate network, and the surface layer is therefore preferably formed at a
25 temperature which minimises crystallisation throughout the thickness of the fibre. Thus the process should be conducted at a temperature below Tc.

The method of the invention by which mineral fibres are treated to form the fibres used in the invention
30 requires exposing fibres containing ferrous iron to a controlled increased temperature which is above the temperature at which oxidation of the iron in the fibres occurs and which is preferably below the temperature at which network crystallisation occurs, i.e., it is below Tc.
35 The temperature is preferably increased in a controlled manner within the range at which oxidation of the iron occurs because increasing the temperature too rapidly, and

in particular if it is increased as a result of a spontaneous exotherm, may give little or no formation of the required calcium magnesium silicate layer on the surface.

5 With normal rock, slag or stone fibres, the oxidation of ferrous to ferric may start in the range 500 to 550°C but it usually starts to a significant extent only at higher temperatures, for instance 550 to 600°C or, often, 600 to 650°C or sometimes even a little higher, for
10 instance in the range 650 to 700 or 720°C. The occurrence of oxidation of ferrous to ferric can be monitored quantitatively by monitoring the increase in weight of the fibres.

15 Throughout the range at which oxidation is occurring, the temperature should be increased in a controlled manner rather than in a random or sudden manner. In particular it is preferred for the temperature to be increased in a controlled manner over a range starting at a temperature which may be as low as 100°C or 50°C below T_g , and is
20 preferably at least 20°C below T_g and which extends up to a temperature of, for instance, at least 30°C and preferably at least 50°C and often up to 100°C above T_g , although preferably the maximum temperature is always below T_c .

25 The controlled increase is preferably performed so that the temperature of the fibres increases by a rate of not more than 30°C per minute and preferably less than 20°C per minute, most preferably 2 to 10°C per minute, e.g., 5°C per minute.

30 The use of a controlled temperature increase maximises the temperature range over which oxidation and outer layer formation can occur before network crystallisation (and embrittlement of the fibres) becomes undesirably significant, and it maximises the extent to which ferrous
35 is oxidised to ferric.

The preferred way of making novel fibres according to the invention is by collecting the fibres as a non-woven

web, and optionally forming this into a batt by cross lapping and compression, or by other conventional techniques, and then exposing the fibres to the desired controlled increase in temperature to cause the required oxidation and surface layer formation. This may be achieved by, for instance, passing the fibres eg as a batt through an oven whose temperature profile is controlled so as to give the batt the required increase in temperature as it passes through the oven. If the batt includes binder or other material which is exothermically combustible, it is preferably burnt off at a relatively low temperature.

The atmosphere in the oven, must be sufficiently oxidising to ensure oxidising conditions always exist in and around the batt, to allow oxidation of ferrous to ferric to occur. The atmosphere can be air or it can be a mixture of oxygen with non-oxidising gas provided that the amount of oxygen is sufficient to maintain oxidising conditions. In practice the oven is usually a forced draft oven.

The amount of oxygen for this purpose can be relatively low and a partial pressure of oxygen of 10^{-2} (0.01) atmospheres seems to be sufficient, for instance in argon, whereas heating at an oxygen partial pressure of 10^{-5} atmospheres is usually ineffective. It therefore seems that the oxygen partial pressure should preferably be at least 0.001 and preferably at least 0.05 atmospheres and generally 0.01 atmospheres or above.

If the desired product has the fibres in unbonded form or as bonded tufts, the process may be conducted on an unbonded batt or primary web instead of on a bonded batt and the treated web or batt may then be converted into the desired product.

The fibres which are treated in the invention, and thus the fibres in the novel products of the invention, are preferably based on stone, rock or slag fibres. Expressed by weight of oxides, such fibres preferably contain at least 2%, and generally at least 3%, 4% or 5% or more

ferrous and may contain as much as 10, 12 or even 15% ferrous. The total iron content of the starting fibres is usually at least 3%, most usually 5 to 10% but can be up to 12 or 15%. Initially some of the iron may be ferric, but
5 the iron is mainly ferrous when the fibres are made under a reducing environment, such as in a cupola furnace.

As regards the other elements, expressed by weight of oxides, the amount of silicon is usually 35 to 55%, often 38 to 50% (i.e., weight percent SiO_2 based on total
10 oxides). The amount of aluminium (as Al_2O_3) is usually 1 to 25%. If it is required that the fibres should be soluble at around pH 7.5 the amount of aluminium is usually from 1 to 10%, usually 1 to 5% (by weight Al_2O_3) but otherwise the amount of aluminium is usually 10 to 25 or
15 30%. Amounts of aluminium of at least 13%, and preferably at least 16% are especially preferred when it is required that the fibres should be soluble at pH 4.5 and typical amounts are 16 to 22%. The amount of calcium is usually at least 8%, often 10 to 20% or more, e.g., up to 30 or 35%
20 (by weight CaO). The amount of magnesium is usually at least 5%, often 8 to 15% or more, for instance up to 20 or 25% (by weight MgO). The fibres may be free of alkali but generally contain alkali (by weight $\text{Na}_2\text{O} + \text{K}_2\text{O}$) in amounts of from zero to 8%, usually 1 to 4% or 5%.

25 The fibres may have been made by any suitable fiberising technique and typically are made by centrifugal fiberisation, for instance using a spinning cup or a cascade spinner process in conventional manner. The fibres may have conventional dimensions for fibres made by
30 centrifugal fiberisation, for instance having a cumulative length based average diameter of less than $15\mu\text{m}$ and preferably less than $10\mu\text{m}$, for instance 2 or $3\mu\text{m}$ to $7\mu\text{m}$. The ratio of the average length to the average diameter is typically above 500:1 and often around 1000:1 to 2000:1.

35 The fibres are usually collected as a web in the presence of a bonding agent to facilitate handling of the collected product. It is desirable to burn off the bonding

agent, and any other exothermically combustible materials, on the fibres before the fibres are subjected to the controlled increase in temperature which is preferably utilised for forming the desired surface layer. Thus, for instance, the binder may be burnt off at, for instance, 500 or 550°C under conditions such that the temperature of the fibres does not exceed, for instance, 600°C or 650°C until the temperature can be controlled accurately by adjusting external heating.

Although the fibres having the surface layer may be present in the novel fibre products in combination with random or deliberate amounts of other fibres, it is preferred that the fibres should be distributed substantially uniformly throughout the mineral fibre product, and that preferably the fibres of the mineral fibre product consist substantially only of the treated fibres.

The novel mineral fibre products of the invention may take various forms. They can be loose fibres, for instance for injection as insulation, or they can be bonded tufts of fibres, but preferred products comprise a batt, i.e., a non-woven of the fibres product which includes a binder or other system for improving the integrity of the batt.

The preferred novel batts preferably have the defined fibres distributed substantially uniformly throughout the batt. By this means substantially uniform sintering properties throughout the batt are achieved.

It is usually desirable for mineral fibre batts to include a system for improving the integrity of the batt. If the system is an exothermically combustible binder, this can incur the disadvantage that exposing the batt to a combustion temperature may cause an exotherm which is greater than is desirable having regard to the properties of the fibres. It is therefore preferred that batts according to the invention should include a non-combustible system for improving the structural integrity of the batt. Such non-combustible systems include conventional

techniques such as needling the batt or sewing the batt with inorganic or other non-combustible fibre, or the non-combustible system may comprise an inorganic bonding agent such as an aluminosilicate or other hydraulic cement.

5 Particularly valuable products of the invention are fire doors and sandwich panels which have been made by forming a treated batt as described above and then partially or wholly enclosing the batt within sheets of
10 sheet material of conventional type for such products, for instance foil or structural sheets (eg of wool, metal, plasterwood or plastics material) which are conventional for fire doors and sandwich panels. These sheets prevent
15 free access of air and thus would be expected to encourage the reducing conditions which have previously been associated with unexpected sintering and collapse, but in
the invention this is avoided as a result of the preformed surface layer on the fibres.

 The modified fibres may be subjected to conventional treatments, for instance they may be provided with surface
20 coatings such as silicone oil or other hydrophobic or dust-reducing coatings. Conventional endothermic materials and other additives may be incorporated in the fire doors or sandwich panels in conventional manner.

 The batts may be of low density, for instance 10 to
25 50kg/m³ or may be of higher density (for instance 50 to 300kg/m³).

 The following is an example.

Example 1

30 A mineral charge is melted in a cupola furnace to form a mineral melt which is then fiberised by a centrifugal cascade spinner to form fibres which are collected as a primary web. This is then cross lapped in conventional manner and consolidated to make a batt containing 0.5% oil and organic binder.

35 The analysis of the fibres (by weight of oxides) is SiO₂ 43.5%, Al₂O₃ 19.0%, TiO₂ 1.1%, FeO 6.0%, CaO 20.3%, MgO 6.6%, Na₂O 2.4%, K₂O 0.3%, P₂O₅ 0.2% and MnO 0.5%.

The batt contains 31.6% shot particles having a diameter above $63\mu\text{m}$ and it has a mean fibre diameter of $4.2\mu\text{m}$, with 16% below $2\mu\text{m}$ and 84% below $7.2\mu\text{m}$. The batt is needled in conventional manner and the binder is cured.

5 The resultant conventional batt is then passed through an oven at a temperature of not more than 500°C in order to burn off the oil and binder and is then passed through a gas blown oven in which the temperature to which the fibres in the batt are subjected is controlled at a value of
10 between 600 and 800°C . For this particular fibre, T_g is 680°C and T_c is 870°C , both determined by DSC.

The atmosphere in the oven is a mixture of argon and air and the temperature to which the batt is subjected in the oven is raised from 620°C to about 800°C at a rate of
15 10°C per minute.

SNMS analysis shows that the final product has an analysis for all elements which is substantially uniform up to the outer $0.5\mu\text{m}$ layer. Between 0.5 and $0.1\mu\text{m}$ there is a gradual increase in the concentrations of magnesium and calcium and a decrease in the concentration of most other
20 elements, and in the outermost $0.1\mu\text{m}$ the concentration of calcium and magnesium is significantly increased with a corresponding reduction in the concentration of the other elements.

CLAIMS

1. A mineral fibre product comprising fibres formed of a silicate network comprising silicon, calcium, magnesium, iron, aluminium and oxygen atoms characterised in that at least 70% of the iron is ferric and the fibres have a core surrounded by an outer surface layer less than $1\mu\text{m}$ thick in which the concentrations of calcium atoms and of magnesium atoms are both at least 1.5 times the concentrations of calcium atoms and magnesium atoms in the total fibre.
2. A product according to claim 1 in which the surface layer merges with the core and has been formed by outwards diffusion of calcium and magnesium ions to the surface of the fibres.
3. A product according to claim 1 or claim 2 in which the surface layer comprises calcium magnesium silicate diopside and/or augite crystals.
4. A product according to any preceding claim in which the surface layer is less than $0.5\mu\text{m}$ thick.
5. A product according to any preceding claim in which the concentration of calcium is at least 2 times, preferably 4 times, the concentration of calcium in the total fibres and the concentration of magnesium is at least 2 times and preferably at least 4 times the concentration of magnesium in the total fibre.
6. A product according to any preceding claim in which at least 95% of the iron is ferric.
7. A product according to any preceding claim in which the fibres contain at least 3% iron, 0 to 8% alkali metal, 35 to 55% silicon, at least 8% calcium, and at least 5% magnesium (as oxides by weight of oxides).
8. A product according to any preceding claim in which the amount of aluminium is from 1 to 5% or 13 to 25% (by weight of oxide based on oxides).
9. A product according to any preceding claim comprising a batt wherein the fibres having the surface layer are distributed substantially uniformly throughout the batt.

10. A product according to any preceding claim comprising a batt comprising the fibres having the surface layer and a non-combustible system for improving the structural integrity of the batt, wherein the system is selected from
5 needling of the batt, an inorganic bonding agent, and sewing of the batt by inorganic threads.

11. A product according to any preceding claim in the form of a fire door or sandwich panel which has been made by forming a batt comprising the fibres having the surface
10 layer and then partly or wholly enclosing the batt within sheets of sheet material.

12. A method of treating mineral fibres formed of a silicate network to improve their high temperature properties wherein the network comprises silicon, calcium,
15 magnesium, iron, aluminium and oxygen atoms, the iron includes ferrous iron in an amount of at least 3% by weight of the fibres, and the method comprises exposing the fibres containing at least 3% by weight ferrous iron under oxidising conditions to a controlled increase in
20 temperature to a temperature which is above the temperature at which oxidation in the iron in the fibres occurs but which is below the temperature at which substantial network crystallisation occurs.

13. A method according to claim 12 in which the fibres are
25 exposed under oxidising conditions to a temperature which is at least $T_g - 50^\circ\text{C}$ (and preferably at least T_g) but below T_c (preferably not more than $T_g + 100^\circ\text{C}$).

14. A method according to claim 12 or claim 13 in which the rate of increase of the temperature to which the fibres
30 are subjected is less than 20°C per minute through the range $T_g - 20^\circ\text{C}$ to $T_g + 100^\circ\text{C}$.

15. A method according to any of claims 12 to 14 in which the fibres are initially formed as a batt or web and the batt or web is exposed to the oxidising conditions in a
35 forced draught oven.

16. A method according to claim 15 in which a batt is formed using an exothermically combustible binder and this

binder is burnt off from the batt whilst maintaining a temperature below the temperature at which oxidation of the ferrous to ferric occurs.

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Mineral Fibre Products

- 5 The properties of mineral fibres are improved by exposure to a treatment which causes migration of CaO and MgO.

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